# FLAMMABILITY CHARACTERISTICS OF METHYLACETYLENE, PROPADIENE AND PROPYLENE MIXTURES[1]

Joseph M. Kuchta, Irving Spolan, and Michael G. Zabetakis

Bureau of Mines, U. S. Department of the Interior
Pittsburgh, Pennsylvania

## INTRODUCTION

Methylacetylene and propadiene are used as welding and cutting fuels, as inter-mediates in chemical production, and as rocket fuels. Mixtures containing these com-bustibles in the gas phase are potentially hazardous because their vapors can decompose exothermally and propagate flame in the absence of oxygen. Heat from surroundings may be sufficient to effect their decomposition and ignition. With increasing tem-perature and pressure their thermal stability may be expected to decrease. The present investigation was conducted to determine the flammability characteristics of gas or liquefied gas mixtures containing these materials together with a hydrocarbon diluent, such as propylene or propane.

The fundamental properties of the methylacetylene decomposition flame at elevated pressures have been studied recently. Hall and Straker (1)[2] report that its burning velocity is about 2 cm/sec between 10 and 40 atmospheres - a relatively low value in comparison to most known flames. They report a critical pressure for flame propaga-tion of 43 psig (lower pressure limit) at about 20° C, in a 4-inch diameter tube. This may be compared with the critical pressure limit of 50 psig, in a 2-inch diameter tube, reported by Fitzgerald (2). Methylacetylene is more stable than acetylene which also forms a decomposition flame. The low pressure limit of acetylene in a 2-inch tube is only about 6 psig (3). Although little information is available on the stability of propadiene, recent experiments indicate that the energy requirements for the ignition of propadiene-methylacetylene mixtures are comparable to those re-quired for the ignition of methylacetylene alone (4).

Like acetylene, methylacetylene and propadiene can be stabilized in a system at a specified temperature and pressure by adding inert gases or hydrocarbons that do not decompose under the given conditions. Fitzgerald (2) reports ethane to be a much better stabilizer than either methane or nitrogen. In the present study, the use of propylene and propane as diluents is examined because of the current interest in these hydrocarbons as stabilizers for methylacetylene and for methylacetylene-propadiene mixtures. The flammability characteristics of such mixtures (vapors) are shown to be sensitive to temperature and pressure, as well as to the size of the reaction chamber.

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[2] Numbers in parentheses indicate references at end of paper.

## EXPERIMENTAL APPARATUS AND PROCEDURE

### Limit of Flammability Measurements

Flammability limits of the methylacetylene-propadiene-propylene system were determined at elevated temperatures and pressures in cylindrical stainless steel bombs measuring 1-, 2-, 4- and 12-inches in diameter, respectively, and in a spherical bomb of 24-inch diameter. The cylinders were about 42 inches long, except for the 12-inch diameter one which was 17 inches long. All of the bombs were insulated with asbestos and heated externally with Nichrome[3] ribbon elements (see figure 1). Chromel-Alumel thermocouples (22-gage), located near the top and bottom of each bomb, were used to follow the heating of the test mixtures introduced into the vessels; thermocouple outputs were measured by a potentiometer. The partial pressure of each mixture component was measured by a mercury manometer or a Bourdon gage which also served to indicate if ignition occurred. A continuous pressure record was obtained during each experiment with an SLM Kistler transducer system whose output was fed to an oscilloscope equipped with a camera. In most determinations, the ignition source consisted of about 1 inch of 38-gage platinum wire located at the bottom of the test vessel.

In preparing for an experiment, a vapor mixture from the liquefied gases was made up in an explosion bomb which had previously been evacuated. To facilitate transfer of the gases from their supply cylinders, the latter were immersed in a water bath maintained at a selected temperature between 20° and 45° C; the explosion bomb was kept at the same temperature. Generally, at least one of the gases was introduced in two increments and alternately with the other gas or gases. To effect mixing, a thermal gradient of about 60 C° was maintained for at least one hour between the top and bottom of the bomb. Calculated mixture compositions, corrected for compressibility, were in close agreement with mass spectrometric analyses made for a few sample mixtures.

After the gases were mixed, the bomb was heated to the desired temperature and the platinum wire was fused. Ignition and extent of flame propagation was determined from the pressure measurements and from the amount of carbon formed. In some instances, complete analyses of the cooled product gases were made. Most of the experiments were performed at 120° C and at pressures of 50 and 100 psig.

The flammability of commercial mixtures (vapor) of liquefied gases was determined in much the same way. However, many of the flammability experiments were conducted at pressures greater than 100 psig and necessitated the transfer of appreciable quantities of the sample mixture to the bomb as a liquid. This was accomplished by first transferring a measured volume of liquid from the supply cylinder to an evacuated stainless steel sphere (523 cc); both were precooled with dry ice. The small sphere was then heated to force the liquid mixture into the bomb where the initial test pressure was controlled by varying the sample volume and bomb temperature. The subsequent procedure was similar to that in the previous experiments.

Two representative commercial mixtures were examined; their compositions are given in table 1. According to the manufacturer's analyses, mixture No. 1 contained about 41 volume-percent diluents, (mostly propane and propylene); mixture No. 2 contained about 32 volume-percent diluents (mostly propane). Mass spectrometric analyses of mixture No. 2 by the Bureau of Mines gave a diluent content of 43 volume-percent for the vapor sample and 29 volume-percent for the liquid sample. This variation can be attributed to the preferential distillation of the lighter diluent components.

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[3] Reference to specific brands, and make or models of equipment is made to facilitate understanding and does not imply indorsement of such items by the Bureau of Mines.

TABLE 1. - Composition of representative commercial mixtures
of liquefied gases (volume-percent)[1]

| | Mixture No. 1 | Mixture No. 2 | | |
| | Mfg.'s analysis (Liquid) | Mfg.'s analysis (Liquid) | BuMines analysis[2] (Liquid) | (Vapor) |
|---|---|---|---|---|
| Methylacetylene | 36.1 | 27 | ⎧71 | ⎧57 |
| Propadiene | 23.3 | 41 | ⎩ | ⎩ |
| Propane | 22.5 | 28 | 22 | 37 |
| Propylene | 10.8 | --- | -- | 2 |
| C$_4$-Carbon cpds. | 7.3 | 4 | 7 | 4 |

1/  Supplied by The Dow Chemical Company.
2/  Mass spectrometric analyses.

The methylacetylene used in this work had a minimum purity of 95 percent and
could contain as much as 4 percent nitrogen according to the vendor's specifications;
mass spectrometer analysis of our sample showed about 2 percent nitrogen present.
The propadiene and propylene were about 97.5 and 99 percent pure, respectively;
propylene was the main impurity in the propadiene.

## RESULTS AND DISCUSSION

### Flammability Limits of the Methylacetylene-Propadiene-Propylene System

Mixtures of methylacetylene and propadiene vapors were found to be flammable
(in the absence of air) in all proportions at 120° C and 50 psig. Addition of propyl-
ene to either of these components produced limit mixture compositions which were de-
pendent upon the temperature and pressure as well as on the vessel diameter. Limit
compositions found at 120° C and at 50 or 100 psig are given in table 2 for vessel
diameters of 1 to 24 inches. The data in table 2 were used to make up the ternary
diagram shown in figure 2. This figure shows the approximate range of flammable mix-
tures for the methylacetylene-propadiene-propylene system under the experimental
conditions noted. In any given vessel, the range of flammable mixture compositions
is greatest with high concentrations of propadiene. For example, propadiene-propylene
mixtures containing up to 31.3 percent propylene are flammable in the 12-inch diame-
ter bomb at 100 psig; 21.9 percent is the limiting propylene concentration for
methylacetylene-propylene mixtures.

The propadiene used in this investigation propagated flame at pressures in ex-
cess of 16 psig at 120° C in a 2-inch diameter bomb; the methylacetylene required
pressures greater than 39 psig. Other investigators have reported similar pressure
limits of 31 psig at 120° C and about 45 psig at 150° C for methylacetylene in 2-inch
and 1-1/4-inch diameter bombs, respectively (2,4). It is not altogether surprising
that methylacetylene should be more stable than propadiene, because the former con-
tains a methyl group that provides increased resistance to thermal degradation.
Pyrolysis experiments (400-650° C) by Meinert and Hurd (5) indicate the same order
of stability for these liquefied gases. They also obtained evidence that methyl-
acetylene first converts to propadiene, which then polymerizes and eventually decom-
poses.

TABLE 2. – <u>Flammability limits of methylacetylene-propylene-propa-
diene mixtures at 120° C in various size vessels.</u>[1]/

| Initial Pressure psig | Methylacetylene Vol.-% | Propylene Vol.-% | Propadiene Vol.-% |
|---|---|---|---|
| | 1-inch ID Bomb (0.47 liter) | | |
| 100 | 92.8 | 7.2 | -- |
| 100 | -- | 19.8 | 80.2 |
| | 2-inch ID Bomb (2.03 liters) | | |
| 50 | 94.7 | 5.3 | -- |
| 50 | -- | 15.3 | 84.7 |
| 100 | 90.4 | 9.6 | -- |
| 100 | -- | 23.8 | 76.2 |
| 100 | 39.4 | 21.5 | 39.1 |
| | 4-inch ID Bomb (7.86 liters) | | |
| 100 | 84.5 | 15.5 | -- |
| 100 | -- | 28.7 | 71.3 |
| | 12-inch ID Bomb (31.0 liters) | | |
| 100 | 78.1 | 21.9 | -- |
| 100 | -- | 31.3 | 68.7 |
| | 24-inch ID Bomb (118.7 liters) | | |
| 100 | >76 | <24 | -- |
| 100 | -- | 32.5 | 67.5 |

1/ Ignition source consisted of 1-inch of 38-gage platinum fuse wire.

The flammable range of the mixtures was noticeably greater at 100 psig than at 50 psig (figure 2). In view of the lower explosion pressure limits given above for methylacetylene and propadiene, it was to be expected that the flammability of the mixtures would be pressure-sensitive under the experimental conditions; even propylene will propagate flame at sufficiently high temperatures and pressures. It was also to be expected that an increase in temperature would widen the limits of flame propagation. In some preliminary experiments at 60° C and 50 psig, mixtures of methylacetylene and propylene failed to ignite in the 2-inch diameter bomb with the ignition source used (1 inch of 38-gage platinum wire); these mixtures ignited readily at 120° C and 50 psig in the same bomb. It is possible that with other ignition sources these mixtures would ignite and propagate flame at the lower temperature (60° C) since ignition energy requirements become most critical near the limiting pressure condition for flame propagation.

The effects of initial pressure, vessel diameter, and mixture composition were also reflected in the pressure measurements. Pressure-time records from experiments in the 1-, 2- and 4-inch diameter bombs with near-limit mixtures of propadiene-propylene and methylacetylene-propylene are shown in figure 3 (A and B); pertinent data from these records are given in table 3. The rates of pressure rise and the maximum explosion pressures developed decrease markedly with a decrease in bomb diameter. For example, the initial rates of pressure rise for the propadiene-propylene mixtures were 60 and 250 psi/sec in 1 and 4-inch diameter bombs, respectively; the

corresponding ratios of maximum explosion pressure to initial pressure were 2.15 and 5.82. Comparable data were obtained with methylacetylene-propylene mixtures. It was evident from these and other results that the heat losses were greatest for the smallest vessel. The quenching diameter for methylacetylene flames is reported to be less than 0.3 cm at 15 psia and 120° C (1); with propylene as diluent, the quenching diameter should be greater under the same conditions.

Explosion pressure-time histories for the flammability determinations conducted in the 2-inch diameter bomb with propadiene and methylacetylene at various initial pressures are also shown in figure 3 (C and D). Maximum explosion pressures were attained more rapidly with propadiene than with methylacetylene, at a given initial pressure. At the explosion pressure limit for propadiene (16 psig), the initial and maximum rates of pressure rise were only 25 and 55 psi/sec, respectively (table 3). These rates, and those obtained for mixtures of these gases with propylene, increased noticeably as the initial pressure and the diameter of the vessel were increased. Because of the relatively low rates of pressure rise observed in most of these determinations, the times required to reach a given pressure were long, as compared to those that are generally observed with combustible-oxidant mixtures in similar bombs. As noted in table 3, the times required to attain maximum pressures were greater than 1 second except in experiments conducted in the 4-inch diameter bomb; these data indicate the slow development and propagation of flame that can be expected in the decomposition of these materials.

The effect of vessel size on the flammability limits of methylacetylene-propylene mixtures at 120° C and 100 psig is illustrated in figure 4. The concentration of diluent (propylene) required to produce limit mixtures increased with an increase in vessel diameter from 1 to 12 inches; above 12 inches the diameter had little effect. The following equations were found to fit the experimental data by the method of least squares for the range of vessel diameters, d, indicated:

Methylacetylene-propylene mixtures:
$$\text{Vol.-\% propylene} = 4.1 + 3.2\,d - 0.14\,d^2; \qquad 1" \leq d \leq 12" \qquad (1)$$
Propadiene-propylene mixtures:
$$\text{Vol.-\% propylene} = 18.3 + 3.0\,d - 0.16\,d^2; \qquad 1" \leq d \leq 12" \qquad (2)$$

The volume percent of propylene is the amount required to obtain a limit mixture.

The vessel diameter effect observed for these mixtures can be attributed largely to the slow flame propagation obtained with these materials. During most of the burning period, the burning velocities probably did not exceed about 2 cm/sec, the value reported by Hall and Straker (1) for pure methylacetylene at 10 atmospheres. With such a low burning velocity, the total heat losses to the walls by conduction and radiation can be significant enough to cause flame extinction. It is to be expected that such effects would be most evident, as is the case here, for the smallest diameter vessels or those with the greatest contact area-to-volume ratio. Judging from the burning velocities and flame temperatures, heat losses due to radiation appear to be very important in the propagation of decomposition flames through methylacetylene and acetylene; observed flame temperatures are much less than values calculated assuming no radiation losses (6,7). However, it has not been established whether such heat losses alone determine the explosion pressure limits of these flames.

The main (cooled) decomposition products from methylacetylene and propadiene were found to be carbon, hydrogen and methane (table 4); small or trace quantities of ethane, ethylene and unreacted gas were also present. Similar results have been obtained with methylacetylene and with acetylene by other investigators (1,2).

TABLE 3. - Pressure data from flammability experiments with methylacetylene-propylene-propadiene mixtures at 120° C and at various pressures.

| Propylene Vol.-% | Bomb Diameter inches | Initial Pressure, $P_1$ psig | Maximum Pressure, $P_2$ psig | Pressure Ratio, $P_2/P_1$ psia/psia | Time to Max. Pressure[1] sec | Initial Rate of Pressure Rise psi/sec | Maximum Rate of Pressure Rise psi/sec |
|---|---|---|---|---|---|---|---|
| | | | | **Methylacetylene** | | | |
| None | 2 | 45 | 233 | 4.18 | 1.295 | 70 | 320 |
| " | " | 100 | 610 | 5.46 | 1.190 | 160 | 1060 |
| | | | | **Propadiene** | | | |
| None | 2 | 16.5 | 68 | 2.67 | 2.070 | 25 | 55 |
| " | " | 18.5 | 89 | 3.17 | 1.335 | 35 | 115 |
| " | " | 22 | 226 | 6.62 | 1.240 | 65 | 440 |
| " | " | 100 | 600 | 5.37 | 1.020 | 150 | 1180 |
| | | | | **Methylacetylene + Propylene** | | | |
| 6.9 | 1 | 82 | 173 | 1.95 | 2.020 | 50 | 60 |
| 5.0 | 2 | 50 | 289 | 4.71 | 1.330 | 90 | 470 |
| 7.9 | 2 | 90 | 458 | 4.53 | 1.310 | 115 | 630 |
| 15.0 | 4 | 100 | 690 | 6.24 | 0.790 | 270 | 1510 |
| | | | | **Propadiene + Propylene** | | | |
| 19.3 | 1 | 100 | 231 | 2.15 | 1.830 | 60 | 100 |
| 21.5 | 2 | 100 | 304[2] | 2.79[2] | 0.945[2] | 160 | 430[2] |
| 27.9 | 4 | 100 | 652 | 5.82 | 0.810 | 250 | 1490 |
| | | | | **Methylacetylene (40.1%) + Propadiene (39.7%) + Propylene (20.2%)** | | | |
| 20.2 | 2 | 100 | 419[2] | 3.78[2] | 1.195[2] | 145 | 810[2] |

1/ Times measured from point of initial pressure rise.
2/ Maximum pressures were not observed.

TABLE 4. - Decomposition products in flammability experiments with methylacetylene-propylene-propadiene mixtures at 120° C and at various pressures

| Initial Propylene Content, Vol.-% | Bomb Diameter, inches | Initial Pressure, psig | Carbon Formed, gms | Gaseous Products (Vol.-%) | | | | | | Hydrogen - Carbon Mole Ratio | | Carbon Conversion[1] % |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | Hydrogen | Methane | Ethane | Ethylene | Nitrogen & Carbon Monoxide | Unreacted Gas | Input | Output | |
| None | 2 | 42 | 6.61 | 71.0 | 25.4 | 0.3 | 0.2 | 1.8 | 1.3 | 1.33 | 1.44 | 71 |
| " | " | 45 | 6.92 | -- | -- | -- | -- | -- | -- | -- | -- | 71 |
| " | " | 60 | 9.19 | -- | -- | -- | -- | -- | -- | -- | -- | 74 |
| " | " | 100 | 13.89 | 73.4 | 19.0 | 0.1 | 0.1 | 1.8 | 5.6 | 1.33 | 1.48 | 73 |
| | | | | Methylacetylene | | | Propadiene | | | | | |
| None | 2 | 16.5 | 2.89 | 61.5 | 29.8 | 0.6 | 2.3 | 0.7[2] | 5.1 | 1.33 | 1.36 | 58 |
| " | " | 18.5 | 3.48 | -- | -- | -- | -- | -- | -- | -- | -- | 67 |
| " | " | 50 | 7.65 | 72.7 | 20.9 | 0.3 | 0.3 | 1.8 | 3.5 | 1.33 | 1.40 | 74 |
| " | " | 100 | 15.69 | 81.7 | 16.3 | 0.1 | 0.1 | 1.8 | 1.8 | 1.33 | 1.42 | 82 |
| | | | | Methylacetylene + Propylene | | | | | | | | |
| 6.9 | 1 | 82 | 1.52 | -- | -- | -- | -- | -- | -- | -- | -- | 40 |
| 7.9 | 2 | 90 | 12.28 | -- | -- | -- | -- | -- | -- | -- | -- | 70 |
| 15.0 | 4 | 100 | 60.68 | 79.1 | 18.2 | -- | -- | 1.7 | 1.0 | 1.43 | 1.75 | 82 |
| | | | | Propadiene + Propylene | | | | | | | | |
| 19.3 | 1 | 100 | 1.80 | -- | -- | -- | -- | -- | -- | -- | -- | 42 |
| 23.3 | 2 | " | 13.90 | -- | -- | -- | -- | -- | -- | -- | -- | 75 |
| 27.9 | 4 | " | 56.81 | -- | -- | -- | -- | -- | -- | -- | -- | 80 |
| | | | | Methylacetylene (50%) + Propadiene (50%) | | | | | | | | |
| None | 2 | 50 | 7.58 | -- | -- | -- | -- | -- | -- | -- | -- | 74 |
| | | | | Methylacetylene (40.1%) + Propadiene (39.7%) + Propylene (20.2%) | | | | | | | | |
| 20.2 | 2 | 100 | 13.55 | -- | -- | -- | -- | -- | -- | -- | -- | 74 |

1/ Mole percent of available carbon converted to free carbon.
2/ Benzene.

However, acetylene generally undergoes more complete decomposition to the elements, (carbon and hydrogen) at the temperatures and pressures employed here. Hydrogen production increased with an increase in initial pressure whereas the methane content decreased. Ethane and ethylene were barely detectable in the products formed at the maximum pressure (100 psig), but they were present in significant amounts (0.6 percent ethane and 2.3 percent ethylene) in the experiment with propadiene at a pressure of 16.5 psig; benzene (0.7 percent) was also found at this low pressure. The same gases form as products of the explosive decomposition of ethylene at elevated temperatures and pressures (8). Hurd and Meinert also report similar products from the pyrolysis of propylene between 600° and 955° C (9); however, they did not find any evidence of aromatic hydrocarbons in the pyrolysis of methylacetylene or propadiene between 400° and 650° C (5).

Figure 5 shows that the amount of free carbon formed was nearly insensitive to mixture composition and increased linearly with initial pressure; these data were obtained at 120° C in the 2-inch diameter bomb. The experimental carbon yield is compared to that which would be expected from the assumed reactions that identify the three curves given in this figure. It is seen that the experimental data fall essentially between the bottom and middle curves which correspond to carbon yields of 2 and 2-1/2 moles, respectively, per mole of methylacetylene ($HC \equiv C\text{-}CH_3$) or propadiene ($H_2C\text{=}C\text{=}CH_2$). However, the gas compositions of the cooled combustion products were not altogether consistent with those of the reactions assumed here.

Material balances based on the complete analyses of the combustion products from methylacetylene and propadiene are given in table 5. As the decomposition products were largely carbon, hydrogen and methane, small quantities of ethane, ethylene, etc. were neglected. Best material balances were obtained in the experiments at 100 psig.

TABLE 5. – Products formed by the explosive decomposition of methyl-acetylene, propadiene, and methylacetylene-propylene mixtures at 120° C and various initial pressures

| Initial Pressure psig | Bomb Diameter inches | Reactants (moles)[1] | Carbon moles | Hydrogen moles | Methane moles |
|---|---|---|---|---|---|
| 42 | 2 | (1)$HC \equiv C\text{-}CH_3$ | 2.16 | 1.08 | 0.39 |
| 100 | " | " | 2.34 | 1.34 | 0.35 |
| 16.5 | " | (1)$H_2C\text{=}C\text{=}CH_2$ | 1.86 | 0.75 | 0.36 |
| 50 | " | " | 2.36 | 1.19 | 0.34 |
| 100 | " | " | 2.54 | 1.44 | 0.29 |
| 100 | 4 | (1)$HC \equiv C\text{-}CH_3$ + (0.175)$H_2C\text{=}CH\text{-}CH_3$ | 2.96 | 2.00 | 0.46 |

1/ Numbers in parentheses indicate moles of reactant.

essentially, only small amounts of additional carbon are needed to obtain agreement between the input and output materials at this pressure. The mole ratio of total hydrogen to carbon was 1.33 for both reactants; it was between 1.36 and 1.48 for their reaction products, including minor constituents such as ethane, ethylene, etc. (table 4). The apparent shortage of carbon may be ascribed to the fact that all of the carbon formed in the reaction vessel was not removed and weighed. The amount of hydrogen and other gaseous products combined or adsorbed in the carbon probably did not introduce a serious error.

The combustion products from an ignition in the 4-inch diameter bomb with 85 per-
cent methylacetylene and 15 percent propylene at 100 psig and 120° C were also analyzed
(table 4). The products were again chiefly carbon, hydrogen and methane, and the
material balance was much like that observed with methylacetylene or propadiene alone
(table 5).

The relative concentrations of hydrogen and methane that were found in the decompo-
sition products may be explained partly by consideration of the decomposition of methane
as follows:

$$2 \ CH_4 \longrightarrow C_2H_2 + 3H_2 \tag{3}$$

$$C_2H_2 \longrightarrow 2C + H_2 \ . \tag{4}$$

According to thermodynamic data, little methane should exist at about 1500° C (10); there-
fore, maximum conversion of methane to carbon and hydrogen should occur at temperatures
equal to or greater than this value. Since the observed flame temperatures for the decom-
position of methylacetylene are about 1300° C (6), noticeable methane concentrations
should then be expected in the end products. With decreasing pressure and vessel size,
the heat losses increase and the ratio of methane to hydrogen should increase, as it
actually did. In comparison, the decomposition of acetylene is associated with higher
flame temperatures which account in part for the small amount of methane that is generally
found in the decomposition of this material.

## Flammability Characteristics of Representative Commercial
## Mixtures of Liquefied Gases

Vapors of commercial mixture No. 1 (41% diluents) did not propagate flame without
air in the 2-inch diameter explosion bomb at temperatures extending from 18° to 187° C
and at corresponding pressures of 80 to 390 psig; the only evidence of reaction was the
presence of small quantities of liquid products and of carbonaceous soot near the ignition
element. In most of these experiments, the ignition element consisted of two platinum
wires (38-gage and 1-inch long) and 50 mg of guncotton.

Commercial mixture No. 2 (32% diluents) showed little evidence of reaction in flamma-
bility tests conducted in the 24-inch spherical bomb at 126° C and pressures up to 116
psig. However, at about 215° C and 285 psig, the mixture decomposed explosively in the
4-inch diameter cylindrical bomb, and the maximum pressure developed was greater than
1000 psig. Ignition occurred without fusion of the ignition source indicating that the
mixture temperature (215° C) was sufficient to ignite the guncotton; spontaneous igni-
tion of the mixture was unlikely in the absence of air at the above temperature and
pressure.

According to the data obtained for various mixtures of methylacetylene, propadiene
and propylene, commercial mixture No. 1 should not be flammable under the experimental
conditions used here because of its high diluent content (22.5% propane, 10.8% propylene,
and 7.3% 4-carbon atom hydrocarbons). Figure 2 shows that this mixture composition does
not fall in the flammable range, assuming that the diluents are as stable as propylene.
However, a moderate increase of the methylacetylene or propadiene concentration would
tend to make the mixture flammable. Moreover, the mixtures will tend to be more unstable
at higher temperatures and pressures. As the composition of commercial mixture No. 2
falls close to the range of flammable methylacetylene-propadiene-propylene mixtures
(figure 2), its behavior at high temperatures and pressures is not surprising.

The ability of paraffin hydrocarbon diluents to stabilize liquefied gases appears to depend partly upon the heat of formation of the diluent. For example, the stability of methylacetylene (2) and acetylene (3) increases with the addition of paraffins of increased molecular weight and decreased heat of formation (negative). The effectiveness of these diluents and of nitrogen decreases in the following order:

Butane > propane > ethane > methane > nitrogen .

Thus, butane and propane should be preferred as stabilizers for these commercial mixtures; they should also be favored over propylene which has a positive heat of formation. The ability of the diluents to absorb heat can also be an important factor here and probably accounts to a large extent for the greater effectiveness observed with hydrocarbons than with nitrogen.

## CONCLUSIONS

Mixtures of methylacetylene and propadiene vapors are flammable in all proportions at an initial temperature of 120° C and a pressure of 50 psig. Nonflammable mixtures are formed by adding propylene and are dependent on such variables as temperature, pressure, vessel diameter, and ignition energy. The range of flammable mixtures increases when the initial pressure is increased from 50 to 100 psig. It increases also when the diameter of the reaction vessel is increased from 1 to 12 inches; above 12 inches the diameter has little effect.

The low pressure (explosion) limits are about 16 psig for propadiene, and 39 psig for methylacetylene at 120° C in a 2-inch diameter bomb. Initial rates of pressure rise following ignition of the test materials are very low and are indicative of unusually low burning velocities. These rates increase with an increase in vessel diameter and pressure.

The end products formed by explosive decomposition of methylacetylene between 42 and 100 psig and of propadiene between 16 and 100 psig are chiefly carbon, hydrogen and methane; methylacetylene-propylene mixtures give similar products. An increase in pressure increases the percentage of hydrogen and decreases the percentage of methane. Decomposition of these liquefied gases to their elements was less complete than that of acetylene at the same conditions.

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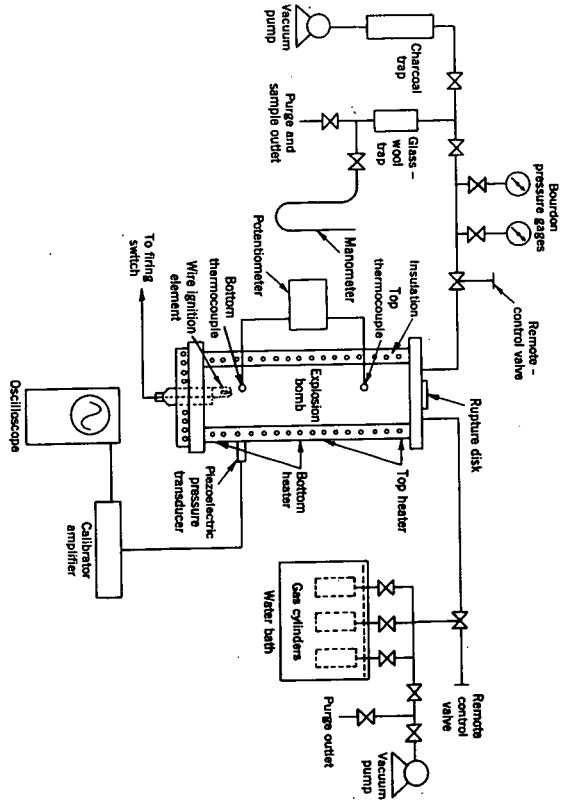
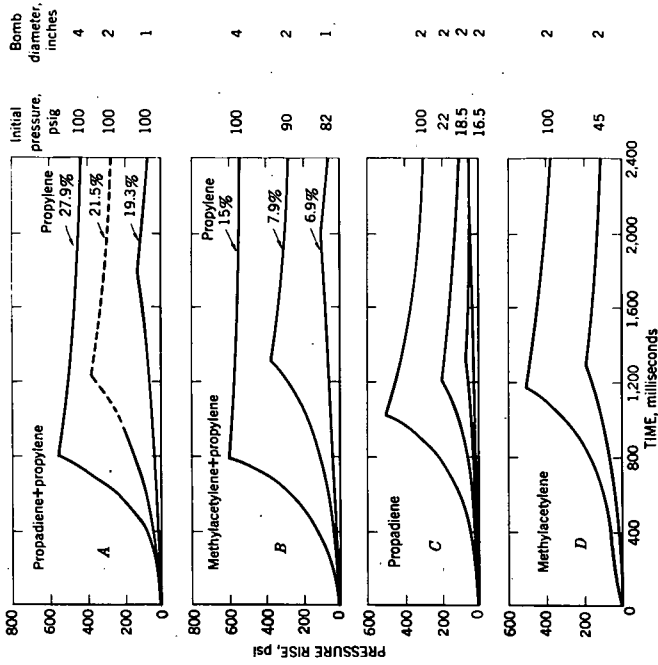Figure 1. - Experimental setup for flammability determinations.

Figure 3. – Pressure-time records following the ignition of methylacetylene, propadiene and propylene mixtures at 120° C and various initial pressures.
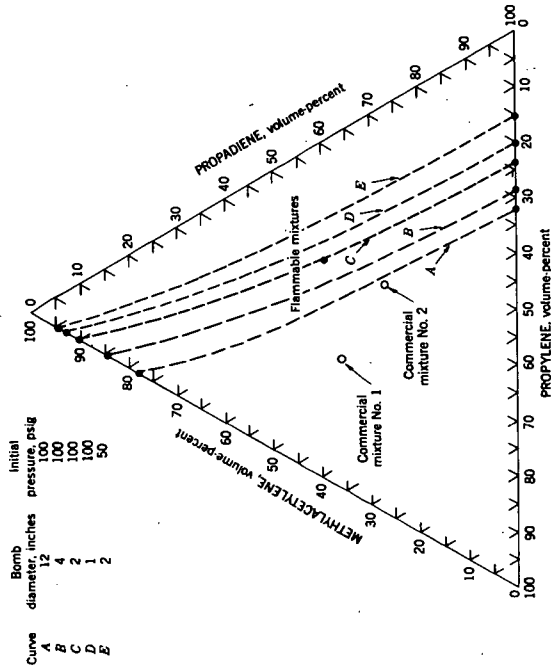
Figure 2. – Range of flammable mixtures for the methylacetylene-propadiene-propylene system at 120° C and at 50 and 100 psig.

PROPYLENE, volume-percent

VESSEL DIAMETER, inches

Limit mixtures of propadiene+propylene

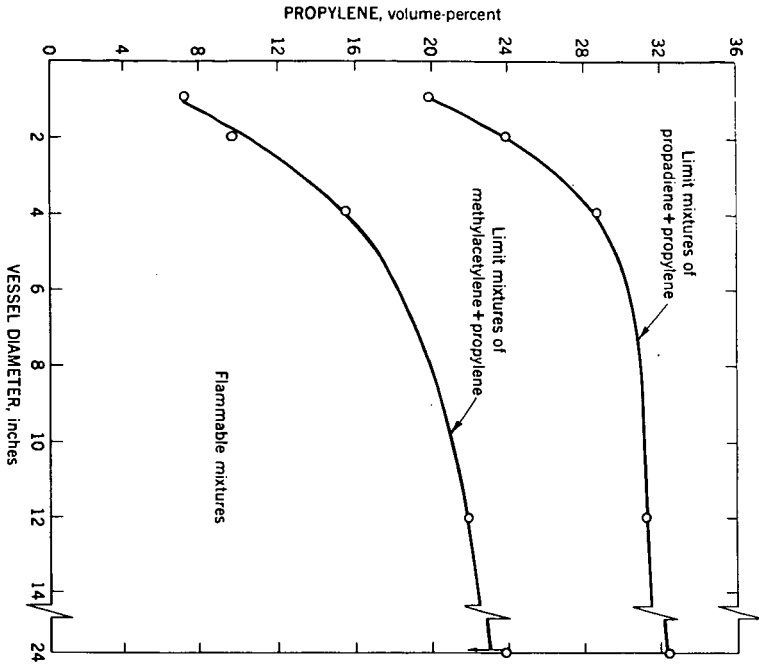Limit mixtures of methylacetylene+propylene

Flammable mixtures

Figure 4. – Effect of vessel diameter on limits of flammability of methylacetylene-propylene and propadiene-propylene mixtures at 120° C and 100 psig.



FREE CARBON, moles

INITIAL PRESSURE, psia

| | Mixture composition, volume percent | | |
|---|---|---|---|
| | C≡C–C | C=C–C | C=C=C |
| ○ | 100 | — | — |
| ■ | 92.1 | 7.9 | 100 |
| ● | — | 23.3 | 76.7 |
| ▶ | 50 | — | 50 |
| ▷ | 19.1 | — | 89.9 |
| ◁ | 40.1 | 20.2 | 39.7 |
| □ | | | |

Assumed reactions

$C_3H_4 \rightarrow 3C+2H_2$
$C_3H_4 \rightarrow 2\frac{1}{2}C+H_2+\frac{1}{2}CH_4$
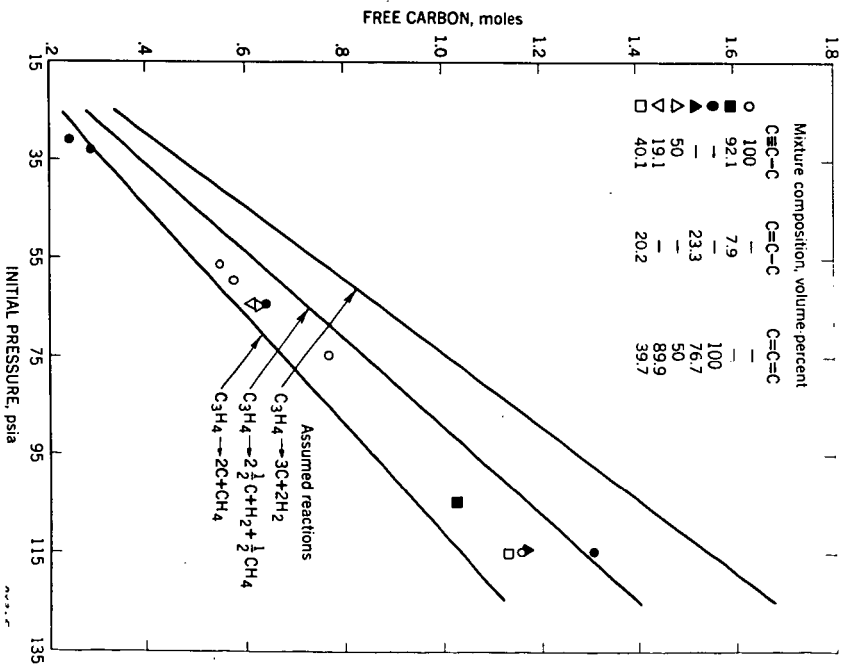$C_3H_4 \rightarrow 2C+CH_4$

Figure 5. – Free carbon formed in explosive decomposition of methylacetylene, propadiene and propylene mixtures at 120° C and various initial pressures (2-inch diameter bomb).